

# Natural and anthropogenic lead in submarine canyons off Portugal

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Lead concentrations in marine sediments off central Portugal have more than doubled since the start of the industrial age in the mid 19<sup>th</sup> century. Especially fine-grained sediments accumulating in deep submarine canyons of Lisbon-Setúbal and Nazaré appear to be enriched in lead. Highest concentrations are generally found in the canyon heads, particularly in the head of the Lisbon canyon, pointing to the densely populated and industrialised Lisbon metropolitan area as the principal source of excess anthropogenic lead.

The global dispersal of contaminant lead, starting with bronze-age ore melting and culminating in the widespread use of leaded gasoline in the 20th century, has been documented from a variety of natural archives including polar ice cores, peat bogs, lake sediments, and estuaries and coastal wetlands. Relatively little attention so far has been given to open ocean sediments, primarily because the pollutant signal is rapidly diluted in an offshore direction through mixing with pre-industrial sediments. An exception to this offshore dilution may be found in submarine canyons. These deep incisions of the continental shelf and slope (Figure 1) often act as traps for fine-grained sediments and associated pollutants entering from the coastal zone. Internal hydrodynamic processes in the canyons carry sediment and contaminants further to the deep ocean, potentially affecting benthic ecosystems over wide areas. We found that anthropogenic lead has indeed penetrated through the entire canyon systems all the way down to 5000 m water depth.

In the project "Lead in Canyons", funded by NWO-ALW, we assessed the dispersal of natural and anthropogenic lead through the Nazaré and Lisbon-Setúbal submarine canyons on the Portuguese continental margin. Both canyon systems head close to the shoreline, whilst their lower ends reach to the abyssal plain at 5000 m depth. The Lisbon-Setúbal canyon system receives direct sediment

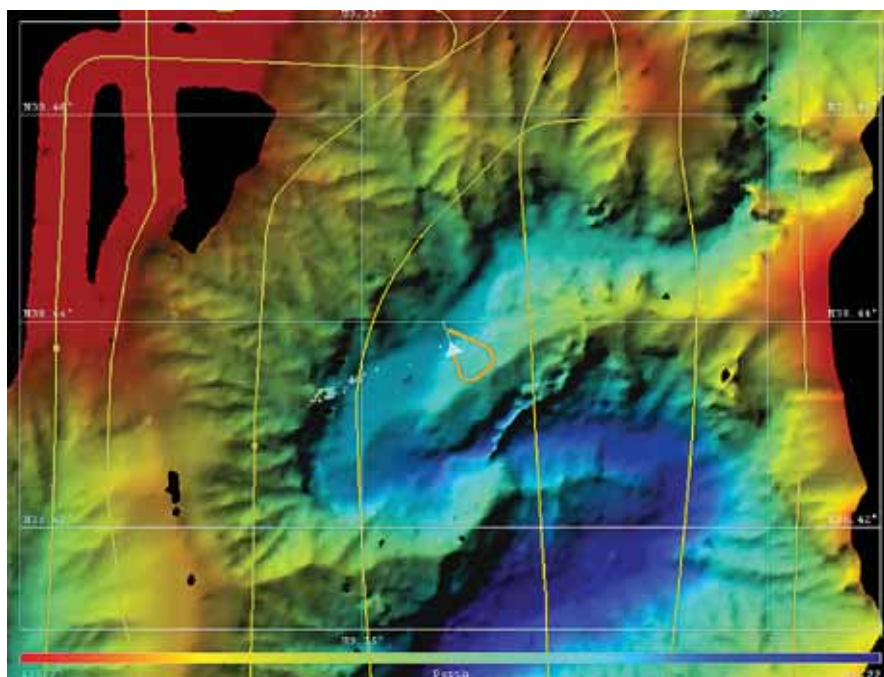


Fig. 1. Multibeam bathymetric image of Lisbon Canyon, showing its 'seascape' deeply incised into the continental shelf and slope

supply by the Tagus and Sado rivers, which both pass through heavily populated and industrialized urban areas close to their river mouths. The Nazaré canyon has no direct connection to a major river system.

For this study we analysed sediment trap samples and sediment cores from depths between 150 and 5000 m, recovered during various cruises with RV "Pelagia" between 2002 and 2007 (Figure 2). Concentrations of total lead and stable lead isotope ratios were determined by ICP-MS. Isotopic ratios allow to distinguish between various sources of lead, both natural and anthropogenic (Figure 3). Sediment age in cores was deter-

mined on the basis of downcore distribution of the radioactive isotope  $^{210}\text{Pb}$ .

Compared to pre-industrial sediment, the lead content in surficial sediment in the Lisbon-Setúbal canyon has increased on average with 54-122%, vs. 25-82% in the Nazaré canyon. Concomitant with the increase in total lead content, a shift in stable lead isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ) provides evidence that the increase was due to an increasing admixture of natural lead superimposed on the natural background (Figure 4). Isotopic signatures of anthropogenic lead reflect the ores from which it is derived and show generally distinctly lower

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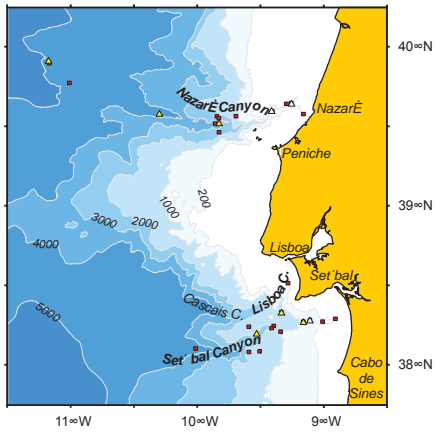


Fig. 2. Samples analysed in this study. Red squares are sediment cores, yellow triangles are sediment traps.

$^{206}\text{Pb}/^{207}\text{Pb}$  ratios and higher  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios than natural lead. For most of the 20<sup>th</sup> century, lead additives in gasoline represented by far the major source of anthropogenic lead, but other industrial sources may again increase in relative importance following the reduction and phase-out of leaded gasoline. The highest anthropogenic lead enrichment observed in the Lisbon-Setúbal area is consistent with its proximity to heavily populated and industrialized areas and with sediment input from the Tagus and Sado rivers. The anthropogenic component generally decreases with increasing water depth. Apart from this geographical effect, lower anthropogenic lead in the Nazaré canyon may also partly be due to the more vigorous hydrodynamic regime in this canyon. A strong internal tide in the upper canyon, and episodic

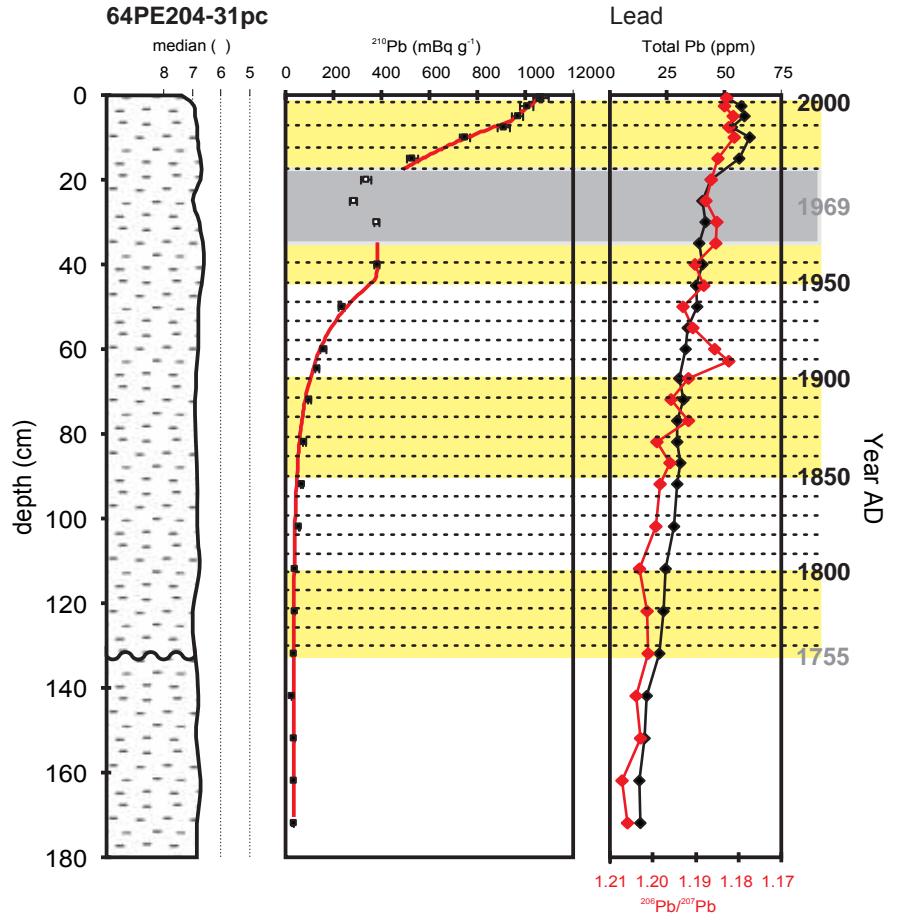


Fig. 3. Historical record of pollutant lead in a Lisbon Canyon sediment core. Age of sediments is inferred from the distribution of the radioactive isotope  $^{210}\text{Pb}$ . Dark gray rectangle highlights a turbidite (event deposition of older material interrupting continuous sediment accumulation) ascribed to the 1969 AD Agadir earthquake. Right panel shows gradual increase in Pb concentrations and shift in isotope ratios, reflecting increasing importance of anthropogenic sources, during the 20<sup>th</sup> century.

down-canyon mass-transport events carrying sediment to the middle and lower canyon, result in mixing of recent contaminated sediment with less contaminated pre-industrial sediment. Although

more diluted, total lead transport down the Nazaré canyon may be more significant than in the Lisbon-Setúbal canyon.

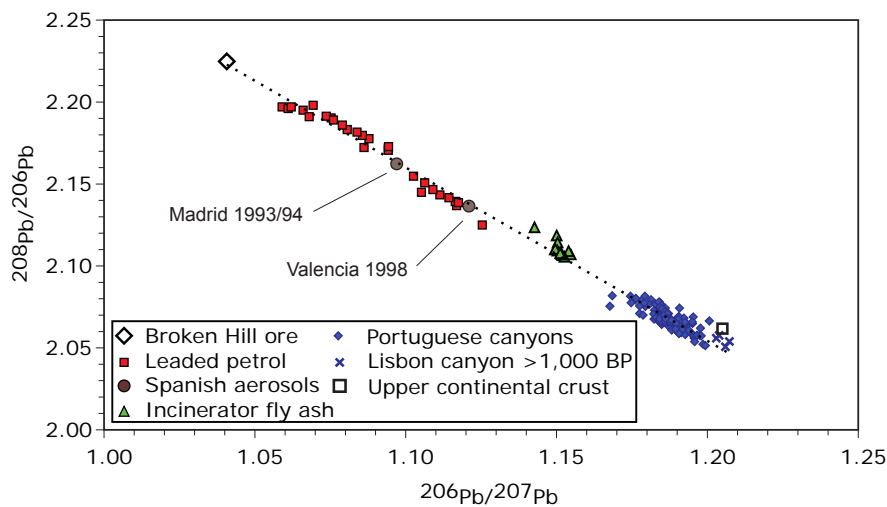


Fig. 4. Three-isotope plot to distinguish natural and anthropogenic sources of lead in Portuguese margin canyons. Blue diamonds: recent samples (surface sediments and sediment trap particulate material) analysed in this study. Black unfilled square: average isotopic composition of upper continental crust. Black crosses: Pre-industrial sediments from a Lisbon Canyon piston core (corresponding to the four deepest data points in Fig. 3). Other symbols correspond to potential sources of pollutant lead.